Critical Current Density of Both F and Cl Doped Filamentary Hg1223 Superconductors

著者	渡辺　和雄
journal or publication title	IEEE Transactions on Applied Superconductivity
volume	9
number	2
page range	1775-1778
year	1999
URL	http://hdl.handle.net/10097/47123

doi: 10.1109/77.784799

Critical Current Density of Both F and Cl Doped Filamentary Hg1223 Superconductors

Tomoko Goto and Takehiro Shimizu
Nagoya Institute of Technology, Nagoya, Japan

Kazuo Watanabe
Institute for Materials Research, Tohoku University, Sendai, Japan

Abstract—**The effect of both F and Cl doping on a transport critical current density (J_c) of the filamentary Hg1223 superconductors was examined to enhance a reproducibility of high J_c. A filamentary precursor $Ba_2Ca_2Cu_3Re_{0.2}O_x$ was fabricated using a solution spinning method and partially melted in an evacuated quartz tube with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(CuCl)_{0.03}O_x$. The addition of BaF_2 and CuCl as a doping vapor source enhanced the reproducibility and stability of the high J_c value at 77 K and 0 T for the filamentary sample owing to the homogeneous fine grain texture.**
Field dependence of the J_c for the filamentary sample was strongly dependent on the post-annealing condition. Although the J_c value for the as-reacted sample and the sample post-annealed in flowing O_2 decreased rapidly by applying the field less than 0.5 T, high J_c value exceeding 10^3A/cm^2 was maintained at 77 K in a field of 10 T by post-annealing in flowing Ar.

I. Introduction

Hg1223 superconductors exhibit the highest T_c value (135 K at ambient pressure) among all superconducting materials so far. As an extremely high J_c value of more than 10^7 A/cm^2 at 77 K and 0 T is reported for Hg1212 thin film, the Hg system superconductors are eminently suitable for high J_c applications at 77 K [1]. Fabrication of stable Hg1223 superconductors into the form of tapes or wires with excellent superconducting properties is necessary for superconducting magnets and power transmission lines. It has been reported that the magnetic properties and chemical stability of Hg1223 ceramics are significantly improved by doping Re to the Hg site [2].

We have studied a fabrication of filamentary Hg based superconductor with Re addition by a two-step method [3], [4]. A controlled vapor/solid reaction process is necessary for preparing Hg-based superconductors by this method. A high J_c value more than 10^4 A / cm^2 at 77 K and 0 T was obtained for both F and Cl doped filamentary Hg1223 sample by controlling the heating conditions [5].

In this paper, the effect of both F and Cl doping on the J_c of the filamentary Hg1223 superconductors was studied to enhance a reproducibility of high J_c. The J_c of the filamentary sample post-annealed under various conditions was also examined in magnetic fields up to 10 T at 77 K.

Manuscript received September 14, 1998.

II. Experimental

Long precursor $Ba_2Ca_2Cu_3Re_{0.2}O_x$ filaments were prepared by dry spinning from a homogeneous aqueous solution that contained mixed acetates of Ba, Ca and Cu, ammonium perrhenate, poly(vinyl alcohol) and organic acids, as reported in a previous paper [3], [4]. The as-drawn precursor filament with a diameter of about 250 μm was pyrolyzed at 450°C at a heating rate of 25°C/h in air in order to remove any volatile components. Then the filament was calcined at 790°C in flowing Ar. The calcined filamentary sample was vacuum-sealed in a fused quartz tube with a doped pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(CuCl)_{0.03}O_x$. The pellet was prepared by a two-step solid state reaction method. Some reacted samples were post-annealed in flowing Ar or O_2.

We measured the electrical resistivity of the filamentary samples by using a standard four-probe method. The samples are about 10 mm in length. Ag was sputtered on four parts of the sample in advance. Silver paint was used to connect the sputtered parts with Ag electrodes. The sample for measurement of the field dependence of J_c was embedded in a substrate using phenolic resin (PR-50702, supplied by Sumitomo Bakelite) and set on a critical current measuring holder. External magnetic fields were applied in a direction normal to the filament length using a helium-free 11 T superconducting magnet at High Field Laboratory for Superconducting Materials, Tohoko University. Currents were passed along the direction of the fiber axis and were normal to the applied magnetic field. A criterion of 1 μV/cm was used for J_c measurements at 77 K.

III. Results and Discussion

A. Effect of vapor source for both F and Cl doping

In a previous paper, the highest J_c value of 1.04 x 10^4 A/cm^2 at 77 K and 0 T was attained for a partially melted filamentary sample with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(HgCl_2)_{0.03}O_x$ [5]. As the reproducibility of the high J_c was very poor, the partial-melting of the filament was examined again. A calcined filamentary $Ba_2Ca_2Cu_3Re_{0.2}O_x$ precursor was reacted in an evacuated quartz tube with a pellet

1051-8223/99$10.00

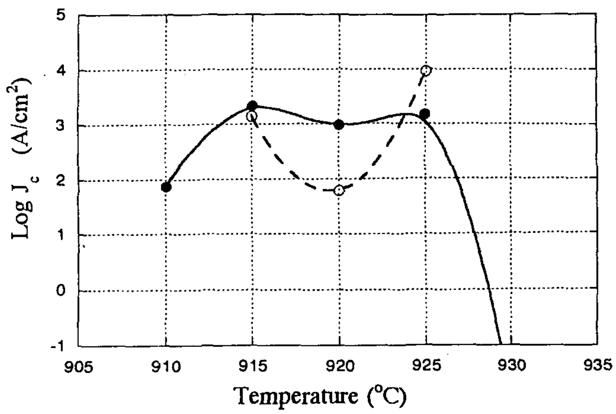

Fig. 1. Relation between the J_c and melting temperature for the filamentary sample partially melted with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(HgCl_2)_{0.03}O_x$.: • as-reacted sample, o post-annnealed sample in flowing O_2.

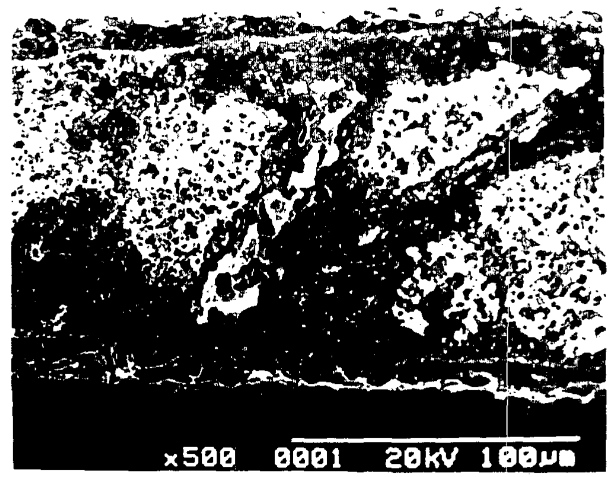

Fig. 2. Polished etched surface on the longitudinal cross-section of the filamentary sample partially melted with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(HgCl_2)_{0.03}O_x$.

of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(HgCl_2)_{0.03}O_x$. The sample was partially melted at various temperatures above 900°C for 45 min and rapid cooled to 890°C and then cooled to 820°C for 6 h, followed by cooling to 30°C for 6 h. A nearly single phase of Hg1223 was detected by X-ray diffraction pattern of the as-reacted filamentary sample. Some reacted samples were post-annealed at 350°C for 15 min and cooled to 250°C at a low cooling rate of 10°C/h, followed by furnace cooling to room temperature in flowing O_2. The J_c at 77 K and 0 T for the filamentary sample partially melted at various temperatures is shown in Fig.1. Although a high J_c value of 9200 A/cm^2 was detected for the sample partially melted at 920°C after post-annealing in flowing O_2, the plots were considerably scattered. The longitudinal cross-section after chemical etching for the sample with high J_c is given in Fig.2. While the filament consists of fine grains, irregular bright domains are observed. The inhomogeneous grain morphology caused the poor reproducibility of high J_c. It was found that the optimum heating conditions, microstructure and the J_c of the filamentary Hg1223 sample were dependent on the vapor source [5]. Therefore CuCl was examined as the vapor source of Cl.

The calcined filamentary $Ba_2Ca_2Cu_3Re_{0.2}O_x$ precursor was reacted in an evacuated quartz tube with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(CuCl)_{0.03}O_x$. The sample was heated at various melting temperatures above 910°C for 45 min and cooled to 820°C at a cooling rate of 50°C/h and held for 10 h and then cooled to 30°C for 4 h. The J_c at 77 K and 0 T for the filamentary sample partially melted at various temperatures is shown in Fig.3. J_c values of more than 10^3 A/cm^2 at 77 K and 0 T are constantly obtained for the filaments partially melted at a temperature ranging from 910°C to 930°C. The addition of both BaF_2 and CuCl for the doping vapor source was improved the reproducibility and stability of high J_c of the filamentary Hg1223 superconductors. Even though the remarkable enhancement of the J_c of the sample was not obtained by post-annealing in flowing O_2, good reproducibility for the J_c value around 8000 A/cm^2 at 77 K and 0 T was obtained. Fig.4 presents the fracture surface and longitudinal cross-section of the filament partially melted. The cross-section of the sample is elliptical in shape and the sample consists of homogeneous fine grains.

B. Field-dependence of J_c for the filamentary sample

The filamentary sample was partially melted at 925°C under the above conditions with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(CuCl)_{0.03}O_x$. Then some reacted samples were post-annealed at 350°C for 15min in flowing O_2. Others were post-annealed at 300°C for 15 min and cooled to 200°C at a cooling rate of 10°C/h, followed by furnace cooling in flowing Ar. The temperature dependence of the electrical resistivity of the filamentary sample post-annealed are shown in Fig.5. These are data of different samples with high J_c. Although there was experimental scatter, a high T_c value was measured for the sample post-annealed in flowing Ar and a low T_c value for the sample in flowing O_2. The as-reacted sample exhibited superconductivity at a zero resistivity temperature (T_c) of 119 K. The T_c for samples post-annealed in flowing Ar and O_2 is 122 K, and 117 K, respectively. The doping level of the as-reacted sample is considered to be overdoped and the level turns to be optimum by post annealing in flowing Ar and to be further overdoped by post-annealing in flowing O_2.

The J_c for post-annealed filamentary samples was examined in magnetic fields up to 10 T at 77 K. The field dependence of J_c was strongly dependent on the post-annealing condition. Fig.6 shows the field dependence of J_c for the samples. For the as-reacted sample and the sample post-annealed in flowing O_2, the J_c value decreases rapidly by applying the field and the superconducting behavior at 77 K disappeared by applying a field of more than 1 T. A remarkable improvement of the field dependece of J_c is observed by post-annealing in flowing Ar.

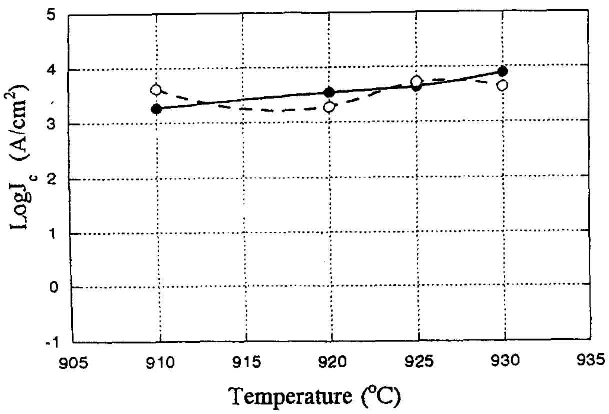

Fig. 3. Relation between the J_c and melting temperature for the filament partially melted with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(CuCl)_{0.03}O_x$.:
• as-reacted sample, o post-annnealed sample in flowing O_2.

A plateau of J_c in the field ranging from 0.5 T to 10 T is observed for the sample post-annealed in flowing Ar and the J_c value of more than 10^3 A/cm^2 (1500 A/cm^2) is maintained at 10 T. The field dependence of J_c for the filamentary samples as-reacted and post-annealed in flowing O_2 is sensitive to the weak-link at the grain boundary which affects J_c in low fields below 0.5 T. While J_c value in a high field region reflects flux pinning, strong links and effective pinning centers in a high field region seem to be introduced by post-annealing in flowing Ar.

Fig.7 and Fig.8 present representative polished and etched longitudinal cross-section of the samples post-annealed in flowing Ar and O_2, respectively. Although as-reacted sample consisted of homogeneous fine grains as shown in Fig.4, the grain morphology was simply varied by post-annealing. A network grain morphology is appeared by post-annealing in flowing Ar and coarse irregular bulk grains for post-annealing in flowing O_2, respectively. The fine grains for as-reacted sample and the coarse grains for the sample post-annealed in flowing O_2 cause to the weak-link behavior.

The field dependence of J_c for F-doped filamentary Hg1223 superconductors was examined in a previous paper. It was found F-doping resulted in a formation of dense liquidus texture and marked improvement in the field dependence of J_c for the sample after post-annealing in flowing O_2. The J_c value more than 100 A/cm^2 was maintained at 77 K in a field of 10 T [6]. The field dependence of J_c for the F and Cl doped sample after post-annealing in flowing O_2 was not improved due to the coarse grain growth, even though both doping F and Cl resulted in higher J_c value at 77 K and 0 T. Post-annealing in flowing Ar for the sample improved the field dependence of J_c.

Several thermogravimetric studies were examined for Hg1223 superconductor. It was noted that the oxygen absorption and desorption temperatures in Hg1223 superconductor below 300°C were sensitive to the oxidizing atomosphere [7]. The pinning mechanism for the present sample by post-annealing in flowing Ar is not clear now. Further work is required.

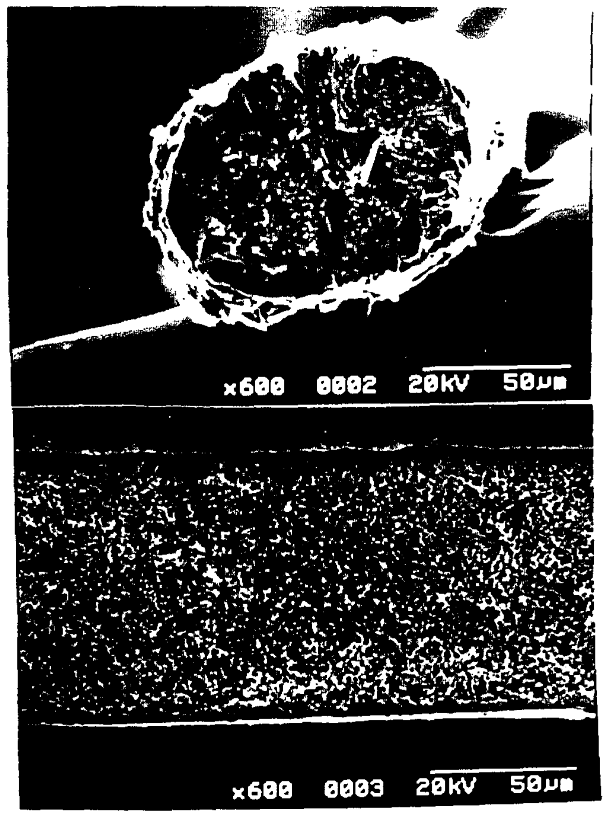

Fig. 4. Fracture surface and polished etched surface on the longitudinal cross section of the filamentary sample partial-melted with a pellet of $Hg_{0.8}Ba_{1.8}Ca_2Cu_3Re_{0.2}(BaF_2)_{0.2}(CuCl)_{0.03}O_x$.

IV. Conclusion

The J_c of both F and Cl doped filamentary Hg1223 superconductors was examined to enhance the reproducibility of the high J_c. The precursor $Ba_2Ca_2Cu_3Re_{0.2}O_x$ filament was fabricated using a solution spinning method and partially melted in an evacuated quartz tube with a doped Hg1223 pellet. Using both BaF_2 and CuCl for vapor source enhanced the reproducibility and stability of high J_c at 77 K and 0 T. The field dependence of J_c was remarkably improved by post-annealing in flowing Ar and J_c value exceeding 10^3 A/cm^2 was maintained at 77 K in a field of 10 T.

References

[1] L. Krushin-Elbaum, C. C. Tsuei and A. Gupta,"High current densities above 100 K in the high-temperature superconductor $HgBa_2CaCu_3O_{6+d}$," *Nature*, vol. 373, pp. 679–681, 1995.

[2] J. Shimoyama, K. Kishio, S. Hahakura, K. Kitazawa, K. Yamaura, Z. Hiroi and M. Takano,"Chemical stabilization and

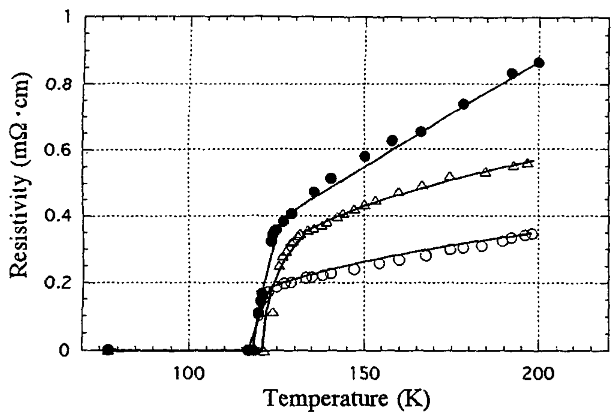

Fig. 5. Resistivity as a function of temperature for the filamentary sample post annealed.:
• as-reacted sample, △ post-annealed sample in flowing Ar, ∘ post-annealed sample in flowing O_2.

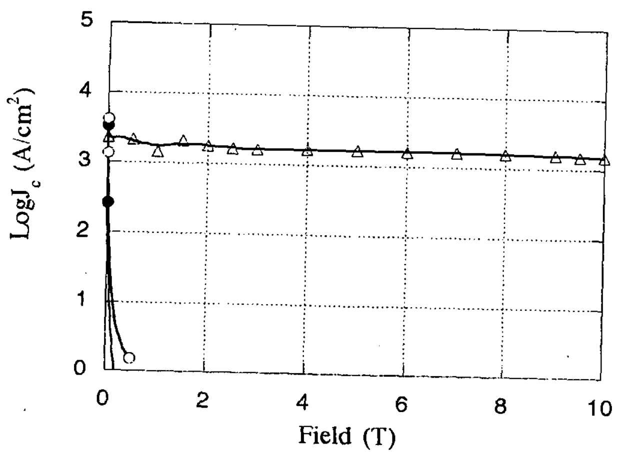

Fig. 6. J_c versus applied field curve at 77 K for the filamentary sample.:
• as-reacted sample, △ post-annealed sample in flowing Ar, ∘ post-annealed sample in flowing O_2.

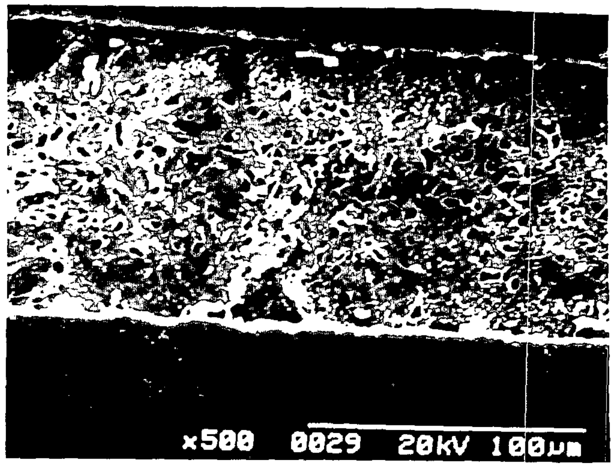

Fig. 7. Polished and etched surface on the longitudinal cross-section of the filamentary sample post-annealed in flowing Ar.

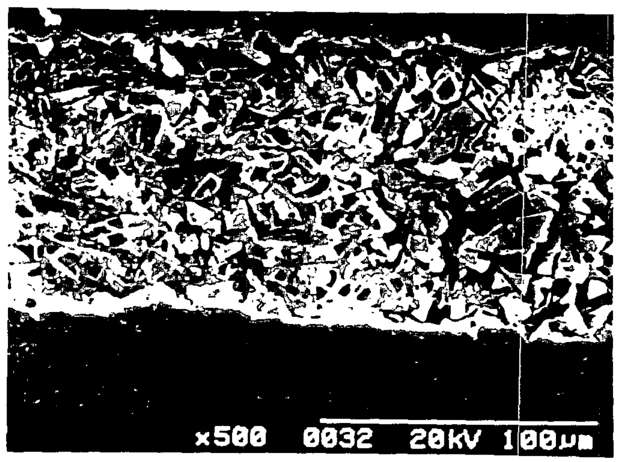

Fig. 8. Polished and etched surface on the longitudinal cross-section of the filamentary sample post-annealed in flowing O_2.

irreversible magnetic behavior of $HgM_2Ca_{n-1}Cu_nO_y$ with M=Sr(Ba) and n=1 to 3," *Advances in Superconductivity*, vol. VII, Yamafuji and Morishima, Eds. Tokyo: Springer, 1995, pp. 287–290.
[3] T. Goto, "Fabrication of superconducting Hg1212 filament by the solution spinning," *Physica C*, vol. 247, pp. 133–136, 1995.
[4] T. Goto, "Fabrication of superconducting Hg1223 filament by solution spinning," *Jpn. J. Appl. Phys.*, vol. 34, pp. L555–L557, 1995.
[5] T. Goto, M. Konishi and M. Tonomura, "Doping effect on partial-melting of $Hg_xBa_2Ca_2Cu_3Re_{0.2}O_y$ filament," in *Advan. in Cryo. Eng.*, vol. 44, pp. 485–492, 1998.
[6] T. Goto, K. Watanabe and S. Awaji, "Field dependence of J_c for F-doped Hg1223 filament," *Jpn. J. Appl. Phys.*, vol. 35, pp. L1404–L1406, 1996.
[7] A. Tokiwa-Yamamoto, A. Fukuoka, M. Itoh, S. Adachi, H. Yamauchi and K. Tanabe, "Thermogravimetric study on $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$ (n=1,2,3) superconductors at various oxygen partial pressures," *Physica C*, vol. 269, pp. 354–360, 1996.